Iraqi Journal of Biotechnology, 2017, Vol. 16, No. 4, 8-14

Biosorption of Chromium ions from Aqueous Solutions by using Date Palm Fibers

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Accepted: April 16, 2017 / **Accepted**: April 30, 2017

Abstract: This research describes the removal of Cr (VI) ions by adsorption on date palm fibers. This plant is locally available in Iraq and nearby countries. Date palm fibers have porous structure as well as rich in carboxyl, hydroxyl, and carbonyl groups which cause the adsorption process. The biosorption of Cr (VI) ions from aqueous solutions by date palm fibers was studied in a batch experiments as a function of, contact time, metal ion concentration, mass of adsorbent and shaking speed. The adsorption data fit well with Langmuir adsorption isotherm model rather than Freundlich model. The adsorption percent was found to be about 93% when the operating parameters are: mixing speed 250 rpm, particle size 100-200 µm, initial chromium ions concentration of 100 ppm and adsorbent concentration 20 g/L. Two isotherm models were tested; Langmuir and Freundlich. Experimental data was found fitted well by Langmuir equilibrium isotherm model.

Keywords: Hexachromium ions, Date palm fiber, Bioabosorption.

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Introduction

As well known, Chromium is widely used in many fields such as chromate manufacturing, metal cleaning and processing, alloy separation industries, leather tanning and electroplating (1). Primarily chromium is present as trivalent and hexavalent in these industrial effluents. Trivalent chromium is relatively less toxic and less mobile (2), Hexavalent chromium is more toxic than trivalent chromium. It is carcinogenic and mutagenic to humans and animals (3). Chronic exposure to Cr (VI) may cause cancer in digestive tract and lungs, therefore, research efforts have been raised that concerned removal of Cr (VI) from industrial wastewaters. Various methods have been used to remove Cr (VI) ions. These methods include reverse osmosis, precipitation, chemical reduction, and adsorption on activated carbon. But most of these methods suffer from some constrains, such as high reagent or energy requirements, incomplete metal removal, generation of toxic sludge. Some of the treatment methods involve high operating and maintenance cost. These constrains make the above chemical methods limited in application (4-7)

In recent years, several studies have been conducted on low cost adsorbents such as wheat straw, tea factory waste and olive leaves. However many of these natural adsorbents either are not locally available or have low adsorbing capacity. Also various types of biomass, including bacteria, yeast, fungi and algae have been tested to be efficient metal removal biosorbent (8-10)

In present work, date palm fibers powder was examined for the removal of Cr (VI) from wastewater. Date palm fibers were selected being rich with carbonyl, hydroxyl and carboxyl groups which responsible for adsorption (19).

Material and Methods

Preparation solutions of Cr (VI)

First one liter solution of Cr (VI) of 500 ppm concentration was prepared (as stock solution) by dissolving 1.416g of potassium dichromate ($K_2Cr_2O_7$) in 1 liter of deionized water (D.W). Then various concentrations of chromium ion solutions were prepared by diluting with appropriate quantity of D.W (11).

Preparation of adsorbent

Date palm fibers were collected and then washed with distilled water (several times) to remove water soluble impurities and surface adhered particles. The washed materials were dried in an oven at 70°C for 12 h. Ball mill was used to crush the dry date palm fibers then after sieved to different particle sizes: (100-200), (200- 300), (300- 400), and (400-500) µm. Diluted H_2SO_4 (3 wt %) was used to activate the powder of date palm fibers. Finally the powder was dried for the next step of the experiments (12).

Characterization of adsorbent

The date palm fiber was characterized using Fourier transforms infrared spectroscopy FTIR. As shown in Figure 1, the band of 1032 refers to existence of C-O groups, while wavenumber of 3330 refer to –OH groups. The bands at 2896cm^{-1} indicates the –H-C groups. The peak around at 1622 cm^{-1} refers to C=O groups. While the band 1428 refer to C=C groups. (12). The bands at 1365cm^{-1} refers to the –COOH groups, while the band 1315cm^{-1} indicates the C=C-H group.

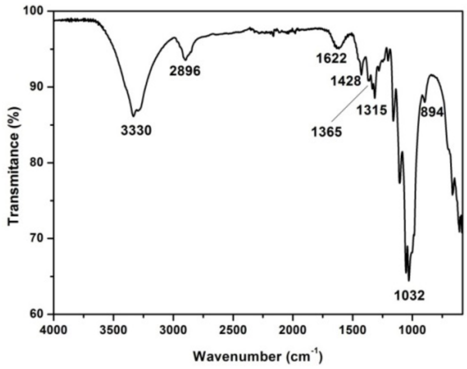

Figure (1): Fourier transforms infrared spectroscopy FTIR spectra of palm date fibers.

Batch experiments

In this work, the studied parameters were particle size, shaking speed, initial concentration of Cr (VI) solution and adsorbent concentration. These experiments were conducted at room temperature. After each experiment the sample was filtered by filter paper (Whatman paper No.42) to separate the residue from the sample. Twenty milliliter of each sample was collected for the next steps of experimental work. The concentration of Cr (VI) after adsorption measured using Atomic adsorption spectrophotometer. The values of operating parameters are shown in the Table 1.

Table (1): Parameters values of experiments

Parameter	values
Adsorbent concentration, (g/L)	5,10,15,20 and 25
Shaking speed. rpm	50,150, 200,250 and 300
Particle size, (µm)	(100-200),(200-300),(300-400),(400-500)
Initial Cr(VI) concentration, (ppm)	100,200,300 and 400

Adsorption percent was calculated by the following equation (1)

$$\text{Absorption}\% = \frac{(C_i - C_e)*100}{C_i} \quad \dots (1)$$

$$\text{Absorption capacity } Q = C_i - C_e \quad \dots (2)$$

Where C_i is initial concentration of Cr (VI) and Ce is final Cr (VI) concentration.

Results and Discussion

Effect of adsorbent concentration

Five values of adsorbent concentration were tested: 5, 10, 15, 20 and 25g/L to show the effect of adsorbent dose on removal efficiency. As shown in Figure 2 the removal efficiency increases as the adsorbent concentration increased and reach maximum value (93%) at 20 g/L. Increasing adsorbent concentration leads to increase in adsorption sites of adsorbent (fibers powder) and hence improve the removal efficiency of Cr(VI) from aqueous solutions. Increasing the concentration above 20 g/L not differ from 20g /L. This is in agreement with that found by Tan *et.al.* (13).

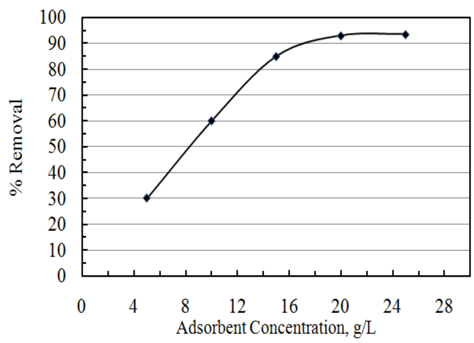

Figure (2): Percent adsorption of Cr (VI) by date palm fibers powder at different adsorbent concentration.

Effect of mixing speed

Five values of shaking speed were taken to show its effect on absorption removal. These values are 50,150, 200,250 and 300. As shown in Figure 3, the percent removal will increase with shaking speed and the best value for shaking speed was about 250 rpm, further increase in shaking speed lead to little decrease in percent removal efficiency. This can be attributed that at high mixing speed extra energy will be liberated and used to form of bonds between the metal ions and the adsorbent. Venditti, *et al.*(14) found that optimum mixing speed occur at 230 rpm when he studied the biosorption of Cr(VI) by Ziziphus Jujuba leaf powder.

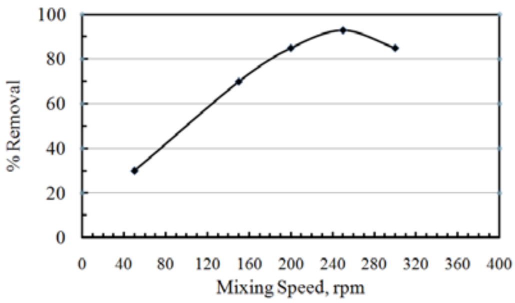

Figure (3): Percent adsorption of Cr (VI) by date palm fibers powder at different shaking speeds.

Particle size Effect

The effect of particle size on removal efficiency was examined. Four different particle sizes were used. They are; (100-200), (200-300), (300-400), (400-500) (µm). As shown in Figure 4, the percent removal is high when the particle size is small. This can be attributed that smaller particles size have greater surface area available for adsorption. This result is in agreement with Uysal *et.al.* (15).

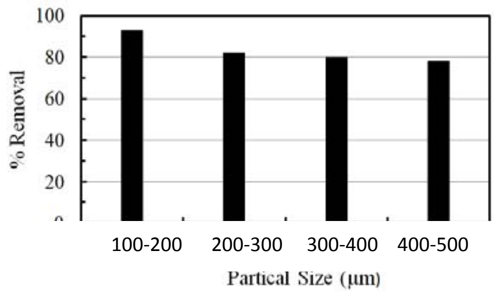

Figure (4): Effect of particle size of date palm powder on adsorption of Cr (VI).

Effect of Cr (VI) concentration

Four initial concentrations were used (100,200,300 and 400ppm) to show the effect of initial concentration of Cr (VI) upon the percent efficiency removal of Cr (VI) ions by date palm fibers. Figure 5 shows that the removal percent decreased as the initial concentration of Cr (VI) ions increased. Since increasing the initial ion concentration will lead to the competitions between these ions on the active sites of the adsorbent surface and hence decrease the percent removal efficiency.

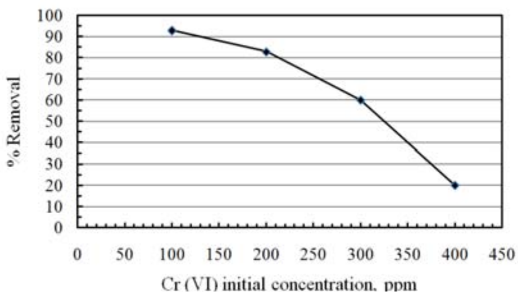

Figure (5): Percent adsorption of Cr (VI) by date palm fibers powder at different initial adsorbent concentration.

Equilibrium Study of Adsorption

The experimental data are analyzed by the Langmuir and Freundlich equilibrium adsorption isotherm (16, 17). The Langmuir isotherm was represented by the following equation:

$$Q_e = \frac{Q_{max}\ m\ C_e}{1+b\ C_e} \qquad \dots (3).$$

Where Qe is the adsorption capacity of the adsorbate (mg/g), Q_{max} is the maximum adsorption capacity (mg/g) and (m) is the Langmuir constant (L/mg). Equation (3) can be written in linear form

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}.m} + \frac{C_e}{Q_{max}} \qquad \dots (4).$$

Plotting Ce/ Qe versus Ce will give a straight line of intercept (1/ Qmax. m) and slope (1/ qmax). Figure 6 shows the plot for adsorption of Cr (VI) at different values of adsorbent concentration.

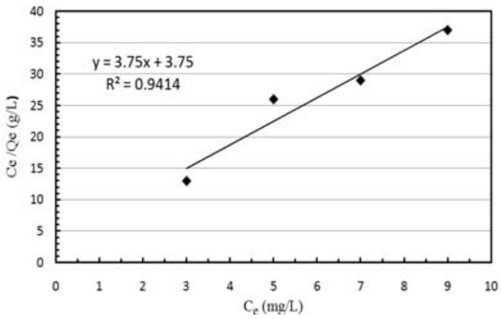

Figure (6): Langmuir isotherm for adsorption of Cr (VI) by data palm fiber powder. (rpm =250, Initial concentration of Cr (VI) = 100 ppm, Particle size = 100 – 200 µm).

Freundlich isotherm is representing by the following equation:

$$Q_e = m_f\ C_e^{\frac{1}{k}} \qquad \dots (5)$$

Where Q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Ce the equilibrium concentration of adsorbate (mg/L), m_f is constant (18). A linear form of the Freundlich equation can be written in a linear form as in the following equation.

$$\ln q_e = \ln m_f + \frac{1}{k}\ln C_e \qquad \dots (6)$$

Plotting (ln Q_e) versus (ln C_e) gives a straight line of intercept (ln m_f).and slope (1/k). Figure 7 shows the plot for adsorption of Cr (VI) at different values of adsorbent concentrations. Table 2 shows the calculated parameter of two models Langmuir and Freundlich equilibrium. Results indicated that the adsorption data fit well with Langmuir adsorption isotherm model (Table 2).

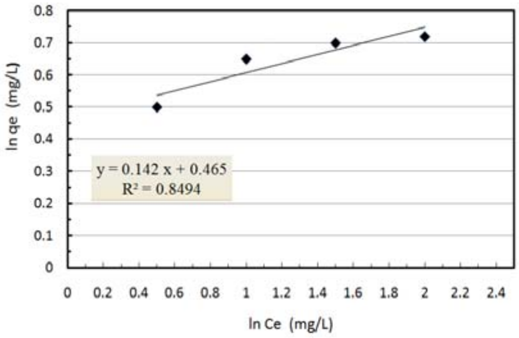

Figure (7): Freundlich isotherm for adsorption of Cr (VI) by data palm fiber powder. (rpm=250, , Initial concentration of Cr (VI) = 100 ppm, Particle size = 100 – 200 µm).

Conclusion

The present work shows that hexavalent chromium ions Cr (VI) could be efficiently removed from aqueous solution by date palm fiber. Many variables affect the absorption process such as adsorbent dosage, shaking speed, particle size and initial metal ion concentration. It was found that the adsorption data fit well with Langmuir adsorption isotherm model. Maximum removal of Cr (VI) was about 93% which occur at the following conditions: particle size cut =100-200, shaking speed 250 rpm, adsorbent concentration=20 g/L and initial concentration of Cr (VI) = 100 ppm.

Table (2): Langmuir and Freandlich models of parameters for adsorption of CR (VI) on date palm fiber powder

Parameter	Langmuir isotherm			Freundlich isotherm		
Adsorbent Conc. (g/L)	Q_{max} (mg/g)	m (L/mg)	R^2	k	m_f	R^2
5	0.1205	0.9765	0.9899	4.6534	1.3987	0.8745
10	0.1098	0.9965	0.9897	4.7648	1.2897	0.9645
15	0.234	1.1765	0.9874	4.8873	1.0786	0.8453
20	0.2871	1.0634	0.9879	5.1876	2.4583	0.8987
25	0.234	1.0887	0.989	5.123	2.012	0.845
Shaking speed rpm	Q_{max} (mg/g)	m (L/mg)	R^2	k	m_f	R^2
50	0.2634	1.1676	0.9567	4.9457	1.3457	0.8743
150	0.2543	1.2443	0.8675	5.0654	1.7732	0.7675
200	0.1765	1.1834	0.9876	5.6754	1.4542	0.8543
250	0.1654	1.0654	0.9943	4.9721	1.4567	0.8453
300	0.2234	1.874	0.9623	3.9567	1.7543	0.7907
Particle size µm	Q_{max} (mg/g)	m (L/mg)	R^2	k	m_f	R^2
100 -200	0.1567	1.3678	0.99567	5.9456	1.4567	0.7112
200- 300	0.1389	1.1678	0.9916	5.1789	1.2613	0.6589
300 – 400	0.2679	1.2512	0.9657	4.8734	1.3835	0.8456
400 -500	0.1741	1.1699	0.9844	4.9938	1.2582	0.8823
Initial conc. Cr(VI) ppm	Q_{max} (mg/g)	m (L/mg)	R^2	k	m_f	R^2
100	0.1568	1.305	0.9912	5.1987	2.1459	0.8198
200	0.1443	1.1623	0.9899	4.5586	1.9683	0.6443
300	0.1987	1.1598	0.9043	4.8895	1.4443	0.7594
400	0.1456	1.144	0.9987	4.765	1.6754	0.5439

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